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(54) Providing a Sheet with Coloured Markings

(57) A sheet 1 is provided with an invisible image of a colour former in area 2. Subsequently a colour reactant in liquid form is applied to the area to cause a visible image to develop. The sheet may be a promotional, self examination or educational device or may be a document to be subjected to an authenticity examination. Preferably the colour former is acidic or phenolic; the colour reactant is a leuco dye in an organic solvent and is applied using felt tip pen 3, a saturated pad or an aerosol. Both the colour former and any other marking may be applied by printing.

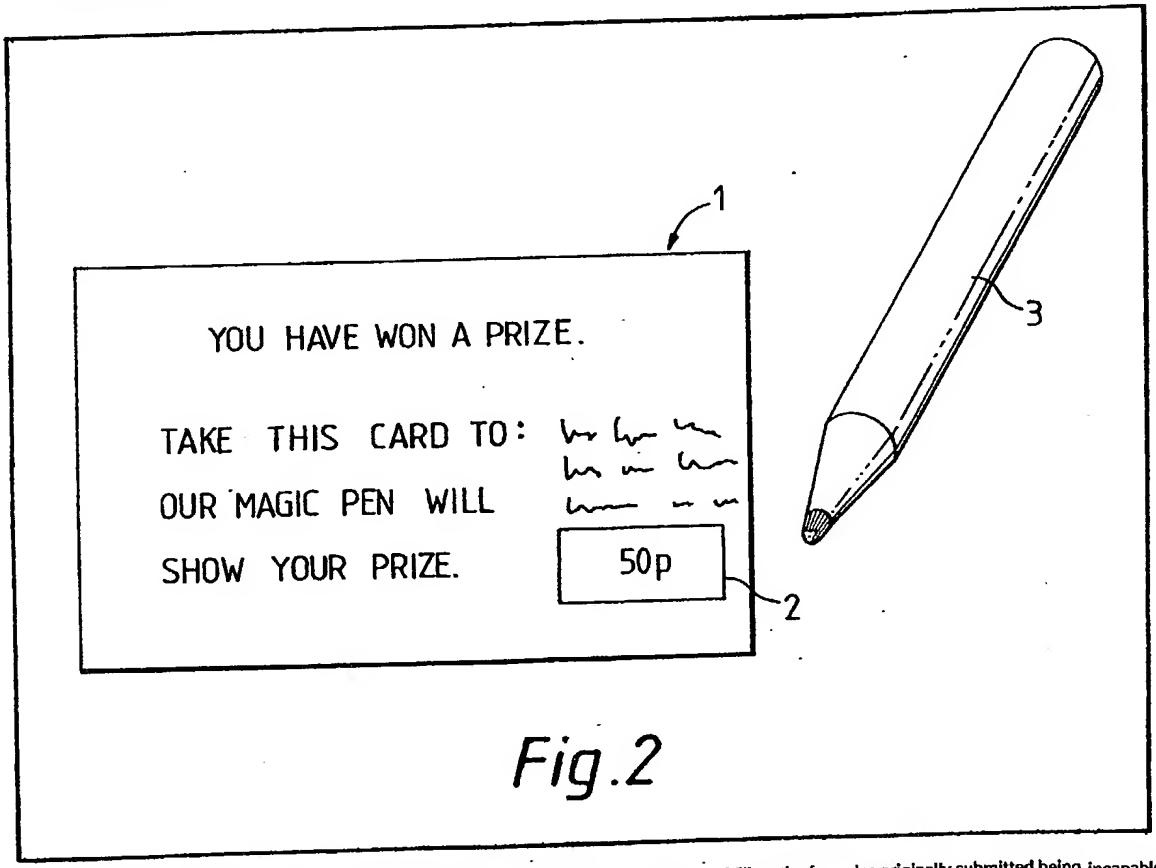

Fig.2

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The Chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.
The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

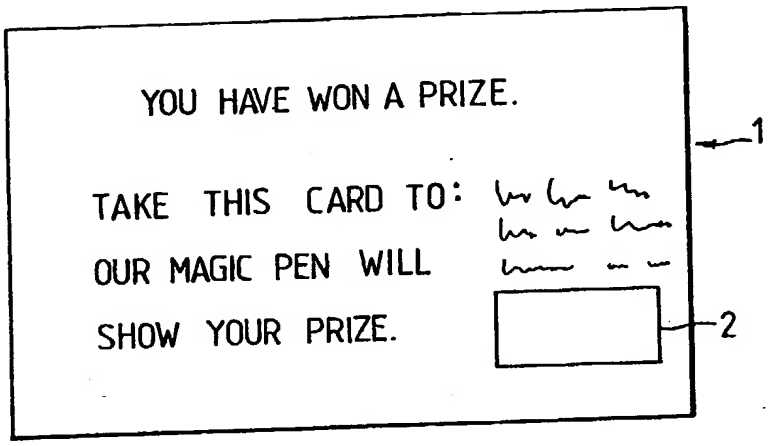

YOU HAVE WON A PRIZE.
TAKE THIS CARD TO:
OUR MAGIC PEN WILL
SHOW YOUR PRIZE.
1
2

Fig.1

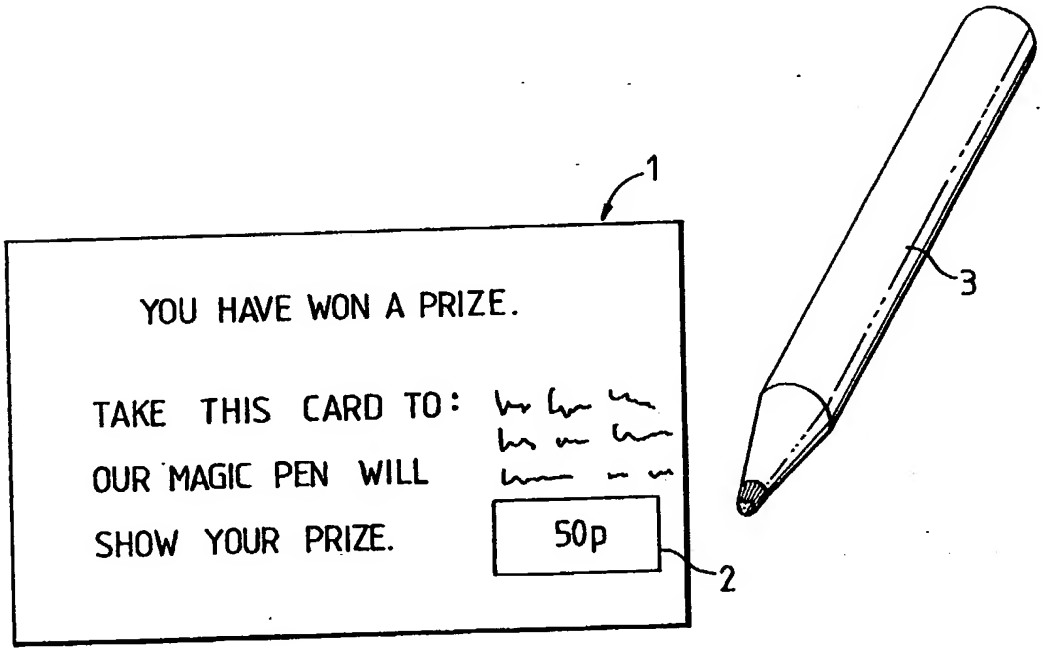

YOU HAVE WON A PRIZE.
TAKE THIS CARD TO:
OUR MAGIC PEN WILL
SHOW YOUR PRIZE.
50p
1
2
3

Fig.2

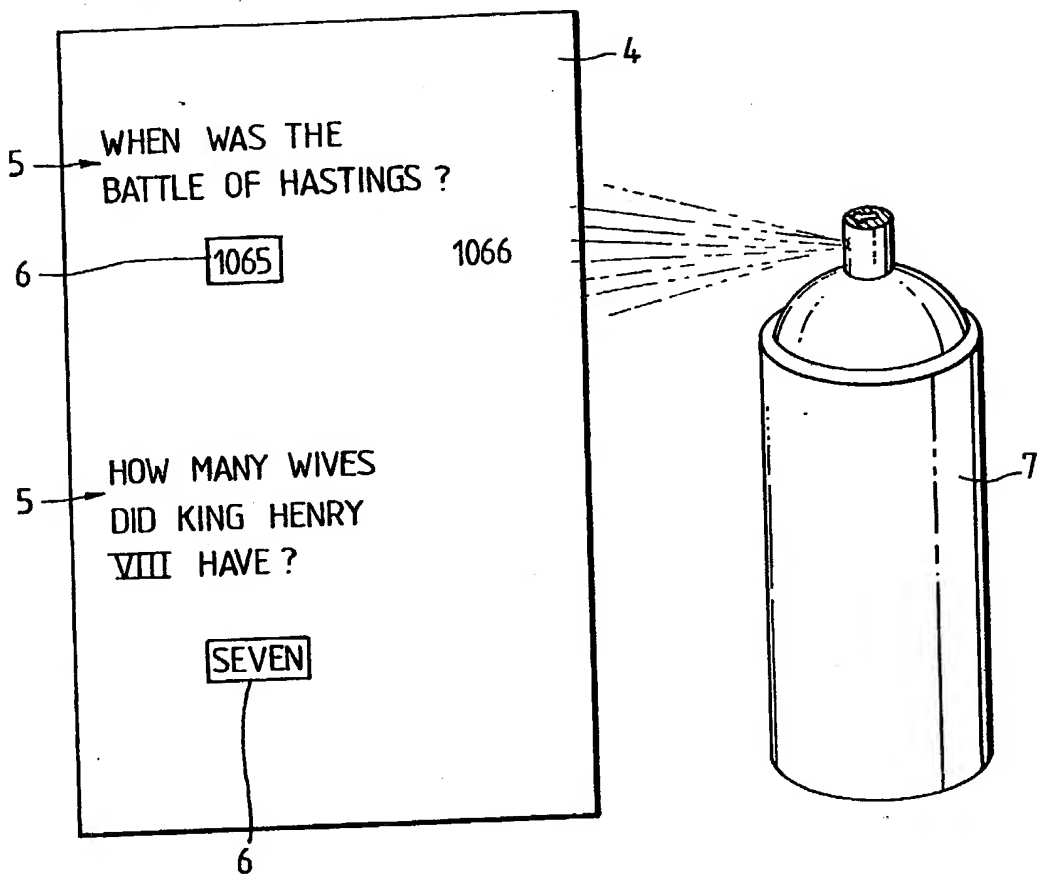

4
5
WHEN WAS THE
BATTLE OF HASTINGS ?
6
1065
1066
5
HOW MANY WIVES
DID KING HENRY
VIII HAVE ?
SEVEN
6
7

Fig.3

SPECIFICATION

Improvements in or Relating to Method of Preparing a Sheet

The present invention relates to a method of preparing a sheet and also relates to a sheet when prepared by the method. More particularly the invention relates to a method of preparing a sheet such that when the sheet is viewed by the naked eye no image can be detected on the surface of the sheet, but subsequently a visible image can be produced merely by applying a liquid to the sheet.

According to the broadest aspect of this invention there is provided a method of preparing a sheet bearing a visible image comprising the steps of providing an area of the sheet having a size and shape corresponding to that of said image with a colour former which, when on the sheet, is substantially undetectable by the naked eye, and subsequently applying to the sheet a liquid comprising a material which reacts with said colour former to provide a coloured image in said area of the sheet.

The colour image may have any colour, for example black although it may be blue, violet or any other selected hue.

Preferably the liquid applied to the sheet is substantially colourless, and the liquid may comprise a solution of a leuco dye stuff in an organic solvent. The organic solvent may comprise alcohol, a ketone or ester or any other convenient volatile solvent such as trichloro-ethane.

It is to be understood that a leuco dye stuff is a material which is invisible, but which reacts with phenol or an acid to be oxidised to form a visible material.

It will be appreciated that the liquid may be applied to the sheet by means of a felt or fibre tip pen, or by means of a saturated pad, or may be applied as an aerosol spray.

It is to be appreciated that the colour former preferably comprises an acidic or phenolic material, the most preferred material being (Bis phenol A) 2,2-bis (4 hydroxyphenol)propane.

Preferably the sheet comprises a promotional or educational or self examination device although alternatively the sheet may comprise a document which is to be subjected to an authenticity examination.

Preferably the method comprises the additional step of printing the sheet with visible images and advantageously said colour former is printed onto said sheet.

According to another aspect of this invention there is provided a sheet, provided in a predetermined area having a size and shape corresponding to the size and shape of a visible image to be developed on the sheet, with a colour former comprising an acidic or phenolic material, said colour former being substantially undetectable on the sheet by the naked eye, the sheet being such that a visible image may be developed in said predetermined area by applying a liquid comprising a material that reacts with said colour former to provide a coloured image.

The colour former may be printed onto the sheet and the sheet may comprise a promotional, educational or self examination device, or a document which is to be subjected to an authenticity examination. Preferably additionally means are provided for applying the said liquid to the sheet, said applying means comprising, for example, a fibre or felt tipped pen or a saturated pad, or an aerosol spray device.

In order that the invention may be more readily understood, and so that further features thereof may be appreciated the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic view of a promotional device comprising a sheet partially prepared in accordance with the present invention;

Figure 2 is a view of the sheet of Figure 1 when prepared in accordance with the present invention; and

Figure 3 is a view of a second sheet in accordance with the invention comprising an educational or self examination device partially prepared in accordance with the invention.

Referring initially to Figure 1 a promotional device in the form of a card 1. The card is printed with visible promotional material. In this particular instance a shop or restaurant may be promoted, cards corresponding to the card illustrated in Figure 1 being distributed to members of the public. The card invites the recipient to attend the particular shop or restaurant to ascertain the precise nature of a prize that has been won. It will be noted that the card 1 is printed with a rectangular box 2. Within this rectangular box 2 there is printed on to the card a colour former. The particular colour former printed on to the card may be selected from a relatively large number of acceptable colour formers, examples of such colour formers being shown in the accompanying table 2. The colour formers are printed in the form of a solution in alcohol, although an ethyl cellulose binder may be included. The arrangement is such that when the colour former has been printed on to the card the printed colour former cannot be detected by the naked eye. It is easy to achieve this if the colour former is printed on to an uncoated m.f. paper or card, and if smoother cards are utilised which may show a texture change associated with the printing of the colour former, then it may be necessary to apply an over varnish comprising a coating of ethyl cellulose which is soluble in the solvent utilised with the leuco dye stuff as will be described hereinafter. Alternatively the box 2 may additionally be printed with visible images which tend to camouflage the printed colour developer. The colour developer is printed only on to a

predetermined area of the box 2, that area corresponding precisely with the visible image to be developed subsequently.

Turning to Figure 2 of the accompanying drawings the card is then illustrated when it has been taken to the premises and when a felt of fibre tipped pen 3 which contains a liquid comprising a material which reacts with the said colour former to provide a coloured image has been drawn across the box 2. Thus the liquid which reacts with the colour former is deposited on the box 2, and as can be seen in Figure 2 the liquid applied from the pen 3 reacts with the colour former to provide a coloured image which, in this case, reads "50p". Thus the person taking the card 1 to the particular shop or restaurant would be awarded a prize of "50p" to be spent at the shop or restaurant.

The liquid contained within the felt or fibre tipped pen 3 comprises an invisible dye, that is to say a leuco dye stuff, which is dissolved in a suitable volatile solvent such as alcohol, a ketone or ester, or a mixture of toluene and alcohol, or trichloro ethane. It is preferred that the solvent is volatile. The solution present in the felt or fibre tipped pen 3 is itself invisible and thus if the solution is deposited on any area of the card which has not previously been provided with the colour former, then no visible coloured image will be formed.

Since the colour former present on the card in the condition shown in Figure 1 is not visible to the naked eye the person receiving the card is not aware of the precise value of the prize awarded. It is only when the pen 3 containing the appropriate invisible dye is used on the card that the prize becomes visible.

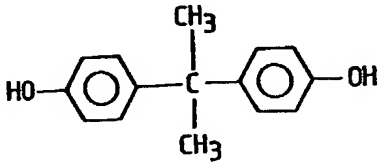
The pen 3 may contain an invisible dye selected from a large number of possible invisible dyes. Examples of such invisible dyes are set out in the accompanying Table 1.

It is to be appreciated that the above description relates solely to one specific example of a promotional device. The invention may be utilised to produce many similar promotional devices.

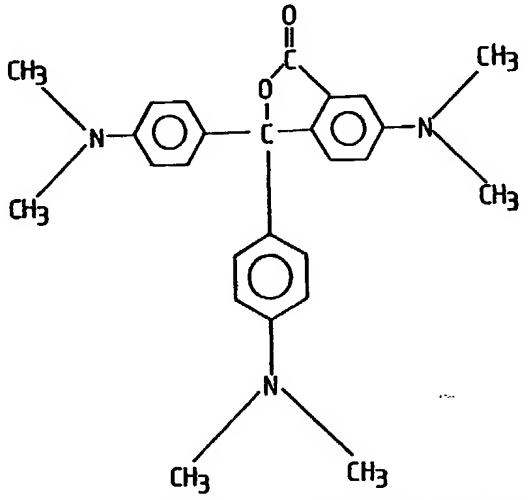
Figure 3 illustrates a second embodiment of the invention in the form of an educational or self examination sheet 4. The sheet carries a number of printed questions 5 and a number of boxes 6 in which candidates have to enter their answers to the questions. The sheet is also printed with colour former so that the colour former is undetectable by the naked eye. The colour former will be of the type described in connection with the embodiment shown in Figures 1 and 2. As shown in Figure 3 an aerosol spray can 7 is provided, this spray can 7 containing an invisible dye of the type generally described above in connection with the embodiment shown in Figures 1 and 2. As shown in Figure 3 the aerosol is being sprayed on an area of the sheet 4 on which the correct answer to the first question has been printed in the colour former. As the aerosol is sprayed so the image of the correct answer becomes visible. It will be appreciated that subsequently the aerosol 7 will be sprayed on a lower region of the sheet 4, thus revealing the correct answer to the second question.

Whilst the invention has been described above with reference to a promotional device and a self examination or teaching device it is to be appreciated that the invention may be of great value in connection with documents which have to be authenticated. Many documents are presently prepared, for example by printing, which have to be authenticated to minimise the risk of forged documents being prepared. Various processes are presently utilised for authenticating documents of this type. However it is envisaged that if a document is printed with a colour former such that the colour former is undetectable to the naked eye, a person attempting to forge such a document would not be aware that the colour former had been provided, and thus whilst a forged copy of the document may at least superficially resemble the original printed document, in order to test the authenticity of the document it would merely be necessary to apply a liquid leuco dye to the appropriate region of the document to be authenticated, for example by drawing on the document with a felt or fibre tipped pen, such as the pen 3 shown in Figure 2 or by spraying the document with an aerosol spray, such as that shown in Figure 7. The colour former would then react with the liquid applied to the sheet to provide an appropriate colour, if the document is genuine, but if the document is a forgery the colour former will not be present and thus it will readily be possible to ascertain the authenticity of such a document.

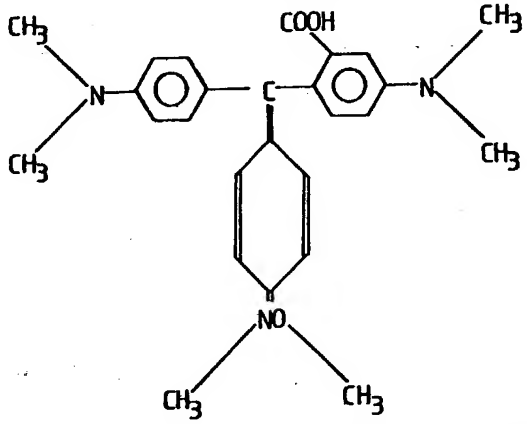
It is to be noted that whilst the colour former and the invisible dye can be selected from a large number of possible materials, the preferred colour former is (Bis phenol A) 2,2-bis(4-hydroxyphenyl)propane. This material has the following formula:—



Preferably the solution containing the invisible dye, that is to say the leuco dye stuff, preferably contains Crystal Violet Lactone (CVL) namely 3,3-Bis P-dimethylamino phenyl)-6-dimethylamino-phthalide. This has the following formula:—



This material is, in the form shown, colourless, but on reaction with the Bis phenol A the material enters a coloured configuration having a blue colour but having the following formula:—



Where the colour former is printed onto a document that is to be subjected to an authenticity test the colour former may be included with a pigmented ink. Thus, to the naked eye, the document would appear to have been printed with ordinary ink of a predetermined colour. However, when a liquid leuco dyestuff is applied to the document, the colour former will react with leuco dyestuff to provide a coloured compound this coloured compound having a colour different from the colour of the pigment in the ink.

Table 1

Invisible Dyes

3,3-Bis (P-dimethylaminophenyl)phthalide (malachite green lactone)
3,3-Bis(P-dimethylaminophenyl)-6-aminophthalide
3,3-Bis(P-dimethylaminophenyl)-6-dimethylaminophthalide (crystal violet lactone)
3,3-Bis(P-dimethylaminophenyl)-6-nitrophthalide
3,3-Bis(P-dimethylaminophenyl)-6-monomethylaminophthalide
3,3-Bis(P-dimethylaminophenyl)-6-chlorophthalide
3,3-Bis(P-dimethylaminophenyl)-6-ethoxyphthalide
3,3-Bis(P-dimethylaminophenyl)-6-diethylaminophthalide
3,3-Bis(P-dimethylaminophenyl)-4,5,6,7-tetra-chlorophthalide
3,3-Bis(P-dimethylaminophenyl)-6-(P-toluenesulphonamide)phthalide
3,3-Bis(dialkylindolyl)phthalide

3-dimethylamine-6-methoxy fluoran
7-acetamino-3-dimethylamino fluoran
7-acetamino-4-dimethylamino fluoran
3-dimethylamino-5,7-dimethylfluoran
3-diethylamino-5,7-dimethylfluoran
3,6'-Bis-B-methoxy ethoxyfluoran
3,6-Bis-B-cyanoethoxyfluoran

Table 1 (cont.).

3-diethylamino-7-dibenzylamino-fluoran
3-diethylamino-7-(N-methylanilino)fluoran
3-diethylamino-7-(N-methyl-P-toluidino)fluoran
3-diethylamino-6-methyl-7-chloro-fluoran
3-dibutylamino-6-methyl-7-chloro-fluoran
3-diethylamino-7-phenyl-fluoran
3-morpholino-5,6-benzofluoran
3',6'-Bis-diethylamino fluoran
3-dialkylamino-6-alkyl-7-alkylamino fluoran

N-2,5-dichlorophenyl leucauramine
N-benzoyl auramine
N-acetyl auramine
Dianisylidene acetone
Dibenzylidene acetone
Anisylidene acetone
P-dimethylaminoazobenzene-o-carboxylic acid
4-aminoazobenzene
4-phenylazo-1-naphthamine
Bis(P-dimethylaminophenyl)methanol
Crystal violet carbinol
Malachite green carbinol
8'-methoxy benzoindolinospiropyran
4,7,8'-trimethoxybenzoindolinspiropyran
6'-chloro-8'-methoxybenzoindolinospiropyran
Benzoindolino-spiropyran
P-dimethylaminostyrylquinoline
Xanthene-9-P-nitroaniline-lactam
9-P-nitroanilino-3,6-bis(diethylamino)-9-xanthenyl-6-benzoicuacid lactam (Rhodamine Blacam)
9-nitroamino-3,6-bis(dimethylamino)-9-thioxanthanyl-6-benzoic acid lactam
3-methyl-2,2-spirobi (benzo (f) cumene)

Table 2
Colour Formers

4-tert-butyl phenol
4-phenylphenol
4-hydroxydiphenoxide & 4-hydroxyphenoxide
α-naphthol
β-naphthol
4-hydroxyacetophenone
4-tert-octyl catechol
2,2'-dihydroxydiphenyl
2,2'-methylenebis(4-chlorophenol)
4,4'-isopropylidene diphenol (Bisphenol A)
4,4'-isopropylidene bis(2-chlorophenol)
4,4'-isopropylidene bis(2,6-dichlorophenol)
4,4'-isopropylidene bis(2,6-dibromophenol)
4,4'-isopropylidene bis(2-methyl phenol)
4,4'-see-isobutylidene diphenol
4,4'-cyclohexylidene diphenol
4,4'-cyclohexylidene bis(2-methylphenol)
2,2'-thiobis(4,6-dichlorophenol)
Hydroquinone
Pyrogallol
Phoroglucine
Phloroglucinol carboxylic acid
Tartaric, succinic acids
Oxalic acid gallic (hydroxy-2-naphthalic acid)
Maleic acid 2-hydroxy-P-talayl acid
Citric acid

Thymol
Resorcinol

Table 2 (Continued)

3,5-xylenol
Catechol
2,2'-methylene bis(4-methyl-6-butylphenol)
2,2'-bis(4-hydroxyphenyl)propane
4,4'-isopropylidene bis(2-tart-butylphenol)
4,4'-sec-butylidene phenol
Clay minerals and oxides
Aluminium oxide, Japanese acid
Clay, kaolin, silica
4-hydroxybenzoate
4,4'-isopropylidene bis(2,6-dimethylaphenol)
4,4'-sec-butylidene bis(2-methylphenol)
4,4'-(1-methyl-n-hyxylidene)diphenol
Methyl-4-hydroxybenzoate
Stearic acid
Salicylic acid
4-hydroxyphthalic acids
o-m or p-chlorobenzoic acid
o-m or p-toluic acid
2-chloro-4-nitrobenzoic acid
2,3-dichlorobenzoic acid
p-isopropyl benzoic acid
2,4-dihydroxy benzoic acid
2,5-dihydroxy benzoic acid
1-naphthoic acid
1-hydroxy-2-naphthoic acid
2-hydroxy-3-naphthoic acid
2-hydroxy-1-naphthoic acid
3,5-dinitrosalicylic acid
3-methyl salicylic acid
2,4-cresotic acid
2,5-cresotic acid
S-tert-butyl salicylic acid
3-phenyl-salicylic acid
3-methyl-5-tert-butyl-salicylic acid
3,5-di-tert-butyl-salicylic acid
3,5-di-tert-amyl-salicylic acid
3-cyclohexyl-salicylic acid
5-cyclohexyl-salicylic acid
3-methyl-5-isoamyl salicylic acid
5-isoamyl salicylic acid
5-nonyl salicylic acid
3,5-di-sec-butyl salicylic acid
Phenoxyacetic acid
Phenylactic acid
Ortho-mercaptobenzoic acid
Alpha-hydroxy phenylacetic acid
Aromatic carboxylic acids and metal compounds, i.e. Zn Sn Al Ni Mg Ca Benzoic Acid o, m & P-chlorobenzoic acids, o, m, p-nitro-benzoic acids, o, m, p-toluic acids, Aromatic carboxylic acids having at least one hydroxyl group ortho to the carboxyl group or in some cases both ortho positions

Phenol, cresol
Phenolic resins.

Claims

1. A method of preparing a sheet bearing a visible image comprising the steps of providing an area of the sheet having a size and shape corresponding to that of said image with a colour former which, when on the sheet, is substantially undetectable by the naked eye, and subsequently applying to the sheet a liquid comprising a material which reacts with said colour former to provide a coloured image in said area of the sheet.

2. A method according to Claim 1 wherein said liquid is substantially colourless.

3. A method according to Claim 1 or 2 wherein said liquid comprises a solution of a leuco dyestuff in an organic solvent.

4. A method according to any one of the preceding claims wherein said liquid is applied by means of a felt or fibre tip pen or by means of a saturated pad.

5. A method according to any one of Claims 1 to 3 wherein said liquid is applied as an aerosol spray.

6. A method according to any one of the preceding claims wherein the said colour former comprises an acidic or phenolic material.

7. A method according to Claim 7 wherein said colour former is (Bis phenol A) 2,2-bis(4-hydroxyphenyl)propane.

8. A method according to any one of the preceding claims wherein said sheet comprises a promotional or an educational or self examination device.

9. A method according to any one of Claims 1 to 7 wherein said sheet comprises a document which is to be subjected to an authenticity examination.

10. A method according to any one of the preceding claims comprising the additional step of printing the sheet with visible images.

11. A method according to any one of the preceding claims wherein said colour former is printed on to said sheet.

12. A sheet provided in a predetermined area having a size and shape corresponding to the size and shape of a visible image to be developed on the sheet, with a colour former comprising an acidic or phenolic material, said colour former being substantially undetectable on the sheet by the naked eye, the sheet being such that a visible image may be developed in said predetermined area by applying a liquid comprising a material that reacts with said colour former to provide a coloured image.

13. A sheet according to Claim 12 wherein said colour former is printed onto the sheet.

14. A sheet according to Claim 12 or 13 wherein the sheet comprises a promotional educational or self examination device.

15. A sheet according to Claim 12 or 13 wherein the sheet comprises a document which is to be subjected to an authenticity examination.

16. A sheet according to any one of Claims 12 to 15 wherein said colour former is (Bis phenol A) 2,2-bis(4-hydroxy phenyl)propane.

17. A sheet according to any one of Claims 12 to 16 in combination with means for applying said liquid to the sheet.

18. A sheet according to Claim 17 wherein said applying means comprise a fibre or felt tipped pen, or a saturated pad.

19. A sheet according to Claim 17 wherein said applying means comprise an aerosol spray device.

20. A method of preparing a sheet substantially as herein described with reference to the accompanying drawings.

21. A sheet substantially as herein described with reference to the accompanying drawings.

22. Any novel feature or combination of features disclosed herein.

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